

Total electronic energy by tight binding approximation and experimental toughness of three different hybrid polymers

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Abstract

We computed by a modified tight binding approximation, the total electronic energy of three different hybrid polymers: $H - SiO_2$, $CH_3 - SiO_2$ and $C_6H_5 - SiO_2$. We made the hypothesis that the structures of these polymers are amorphous. Computational results regarding the total electronic energy and experimental data [1] on the toughness of these three hybrid polymers were compared. A good qualitative agreement was found between computations and experiments.

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Since few years, organic inorganic hybrid materials issued from sol-gel process and an organic polymerized part are more and more intensively studied. They offer a very innovative way to develop a wide variety of new materials because of their structure at the nanometer scale which combines the properties of an organic and an inorganic entity.

On an industrial point of view, these materials are more used as layers such as protective coatings [2], materials with high transparency [3] transistors [4], luminescent diodes [5], solar cells [6], waveguides [7] and photochromic coatings [8].

Hybrid materials may be classified into two families. The class I family corresponds to hybrid materials where the organic part is embedded in an inorganic network. The interactions between the mineral and the organic parts are weak essentially Van der Waals, hydrogen bonds and electrostatic interactions [9]. The class II corresponds to the existence of chemical bonds (covalent or ionic-covalent) between the organic and the mineral part of the network [9]. The synthesis of class II hybrid polymers has been initiated simultaneously by the sol gel scientists and the polymer scientists.

The sol gel process is a method to obtain hybrid polymers: one would have to incorporate to the sol inorganic precursors and organic compounds with functionalities which can be plugged to the inorganic part of the gel. This may lead to hybrid nanomaterials [10].

We deal here with class II hybrid polymers containing the species: Si, C, O and H . This type of polymers may be obtained by the sol gel process. In this particular type of polymers containing only sp^2 and sp^3 bonds it is possible to use a tight binding approach to compute the total electronic energy.

Our tight binding method has been modified in order to take into account hybridization i.e. the σ and the π valence electrons which enter a covalent bond. The tight binding method depends only on the connectivity of the atoms which enter a structure and not on the real distribution of the atoms in space. In a previous work, we showed that the connectivity of hybrid polymers containing only Si, C, H and O was amorphous [11].

The aim of this study is to compare the computed toughness of three kinds of hybrid polymers to the toughness of the same kind of materials obtained in the literature.

Let us introduce our tight binding approach. Let us remind that this is a one electron model, each electron moves in a mean potential $V(r)$ which represents both the nuclei attraction and the repulsion of other electrons. σ and π electrons are separately treated :

If the molecular orbital σ is given by:

$$|\Psi\rangle = \sum_{i,J} a_{iJ} |iJ\rangle \quad (1)$$

and the energy origin taken at the vacuum level, the Hamiltonian can be written as, in the case of sp^ν ($\nu = 1, 2, 3$) hybridization:

$$H_\sigma = E_m \sum_{i,J} |iJ\rangle \langle iJ| + \Delta_i \sigma \sum_{i,J,J' \neq J} |iJ\rangle \langle iJ| + \beta_\sigma \sum_{i,i' \neq i,J} |iJ\rangle \langle iJ| \quad (2)$$

(i and i' are first neighbours) where E_m is the average energy: $E_m = (E_s - \nu E_p)/(\nu + 1)$, E_s and E_p are the atomic level energies, β_σ is the usual hopping or resonance integral in tight binding theory (interaction between nearest neighbour atoms along the bond), Δ_σ is a promotion integral (transfer between hybrid orbitals on the same site): $\Delta_\sigma = (E_s - E_p)/(\nu + 1)$.

The Hamiltonian of the π bonds is given by:

$$H_\pi = E_p \sum_i |i\rangle \langle i| + \beta_\pi \sum_{i,i' \neq i} |i\rangle \langle i'| \quad (3)$$

with $|i\rangle$ the π orbital centered on atom i , and β_π the hopping integral for π levels.

We need only 3 parameters: β_σ , β_π , and Δ_σ for the homonuclear model which represent in fact the average potential $V(r)$ and which take into account the nuclear attraction and the dielectronic interactions [12]. But due to the fact that we only take into account on average the nuclear and dielectronic interactions, we can only compare clusters with the same number of atoms.

The numerical values of the parameters are given in table 1.

In the following are the computational results compared to experiments. We computed the total electronic energy for three types of hybrid polymers: $H - Si$, $CH_3 - Si$ and $C_6H_5 - Si$ for the organic part of the hybrid polymers and $Si - O - Si$ for the inorganic part of the hybrid polymer.

In figure 1, one may see the typical structure that we used for the tight binding calculation in the case of an amorphous hybrid polymer. The picture shows a planar molecule but this may be folded and the angles between different atoms may not be equal to 90° and the length of the bonds may be changed depending on the type of atoms [13, 14, 15, 16]. Thus it represents an amorphous structure. Here $R = H, CH_3$ or C_6H_5 . Let us remark that there are sp^2 bonds in the C_6H_5 cycle.

In figure 2, we showed the total electronic energy as a function of the number of atoms in the polymer.

Figure 3 shows again the total electronic energy but as a function of the number of valence electrons (not differentiating the sp^2 and sp^3 bonds i.e. the π and the σ electrons).

Finally, table 2 is a comparison of the toughness of the three different hybrid polymers that we computed here, with the experimental data coming from the literature [1].

We made a linear regression of the results shown in figure 3. The result is that the slope of the total electronic energy as a function of valence electrons is the same within computational error for $H - Si$ and $CH_3 - Si$: $22,0 \pm 0.6eV$. Thus the difference of total electronic energy cannot be differentiated by the the number of valence electrons. But, in the case of $C_6H_5 - Si$, the slope given by the linear regression is $20.9 \pm 0.6eV$. We can conclude from figure 3 that the total electronic energy is larger for the case $C_6H_5 - Si$ than for the two other cases of hybrid polymers.

This result may be related to mechanical properties of such material: the toughness of the amorphous hybrid material is the largest; indeed, the total electronic energy is related to the toughness of the electronic bonds within the structure, so the toughness of the electronic bonds can be linked to the mechanical toughness of the material.

Let us examine more in details the total electronic energy as a function of the total number of atoms. We made once again a linear regression over the three different hybrid polymers. For $H - Si$, we obtained:

$$E = 217,4 - 89.7.N_{at} \quad (4)$$

For $CH_3 - Si$ the result is:

$$E = 382,5 - 79,6.N_{at} \quad (5)$$

and finally for $C_6H_5 - Si$, we obtained:

$$E = 368,5 - 72,3.N_{at} \quad (6)$$

where E is the total electronic energy in eV and N_{at} is the total number of atoms. We see that in the case of $C_6H_5 - Si$, the slope is the largest (do not forget the minus sign), therefore, the stability of such hybrid polymer is the smallest compared to the two others. This is in good agreement with the linear regression of figure 3 given before. But, in figure 3 one cannot distinguish the stability of $H - Si$ and $CH_3 - Si$. With the results of figure 2,

this is done: $CH_3 - Si$ is less stable than $H - Si$ as its total electronic energy is larger for a large number of atoms.

We compared the toughness of our computed hybrid polymers with the results given by literature [1]. The results are given in table 2. As one may see in table 2, the total electronic energy and the experimental toughness follow the same tendency. The toughness of $H - Si$ and $CH_3 - Si$ are in good agreement with the computed total electronic energy. Regarding the results of $C_6H_5 - Si$, one cannot make a direct comparison: the comparison cannot be quantitative. For that we calculated the ratio E/T and we see that for the cases of $H - Si$ and $CH_3 - Si$, the ratio is almost the same, while for the case of $C_6H_5 - Si$ it is three times larger.

Indeed, the total electronic energy of $C_6H_5 - Si$ is the largest (thus the less stable) but the numerical results compared to the toughness can only be compared qualitatively. The explanation of this feature is that experimentally [1] the presence of the C_6H_5 group leads to a less connected array in the final polymer obtained by sol gel [1]. As we did not take into account this type of phenomenon (the connectivity was an hypothesis of our numerical computation), we did only compute the total electronic energy of an ideal structure. In real systems obtained by sol gel, 20% of the species are not totally condensed in the case of $C_6H_5 - Si$ and 5% to 10% are not condensed for $H - Si$ and $CH_3 - Si$ [1]. This explains the difference between computation and experiments.

To conclude, we may say that the toughness of experimental and numerical such hybrid polymers may be compared qualitatively: the toughness (and E) of $H - Si$ is the largest followed by $CH_3 - Si$ and finally the smallest toughness is obtained for $C_6H_5 - Si$.

A final conclusion is that we made a comparison between the toughness of three different hybrid polymers and the total electronic energy obtained by a modified tight binding method. The result is that the toughness follows the same tendency as E but only qualitatively. This is due to experimental characteristics of the sol gel process which is used to obtain these polymers which we do not take into account in our computations.

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atom/parameter	E_σ	E_π	β_σ	β_π
H	13.6	0.0	15.05	0.0
C	19.45	10.74	7.03	3.07
O	32.37	14.96	12.0	5.0
Si	14.96	7.75	4.17	0.8

TABLE I: Parameters for the tight binding calculations

hybrid polymer	total electronic energy per mol H (J)	experimental toughness T (MPa.m ^{1/2}) [1]	ratio H/T
$H - Si$	$-3.3.10^6$	0.33 ± 0.05	-10^7
$CH_3 - Si$	$-2.98.10^6$	0.32 ± 0.05	$-0.93.10^7$
$C_6H_5 - Si$	$-2.71.10^6$	0.09 ± 0.01	-3.10^7

TABLE II: Comparison between the total electronic energy of the three hybrid polymers computed by tight binding and experimental toughness from literature [1]

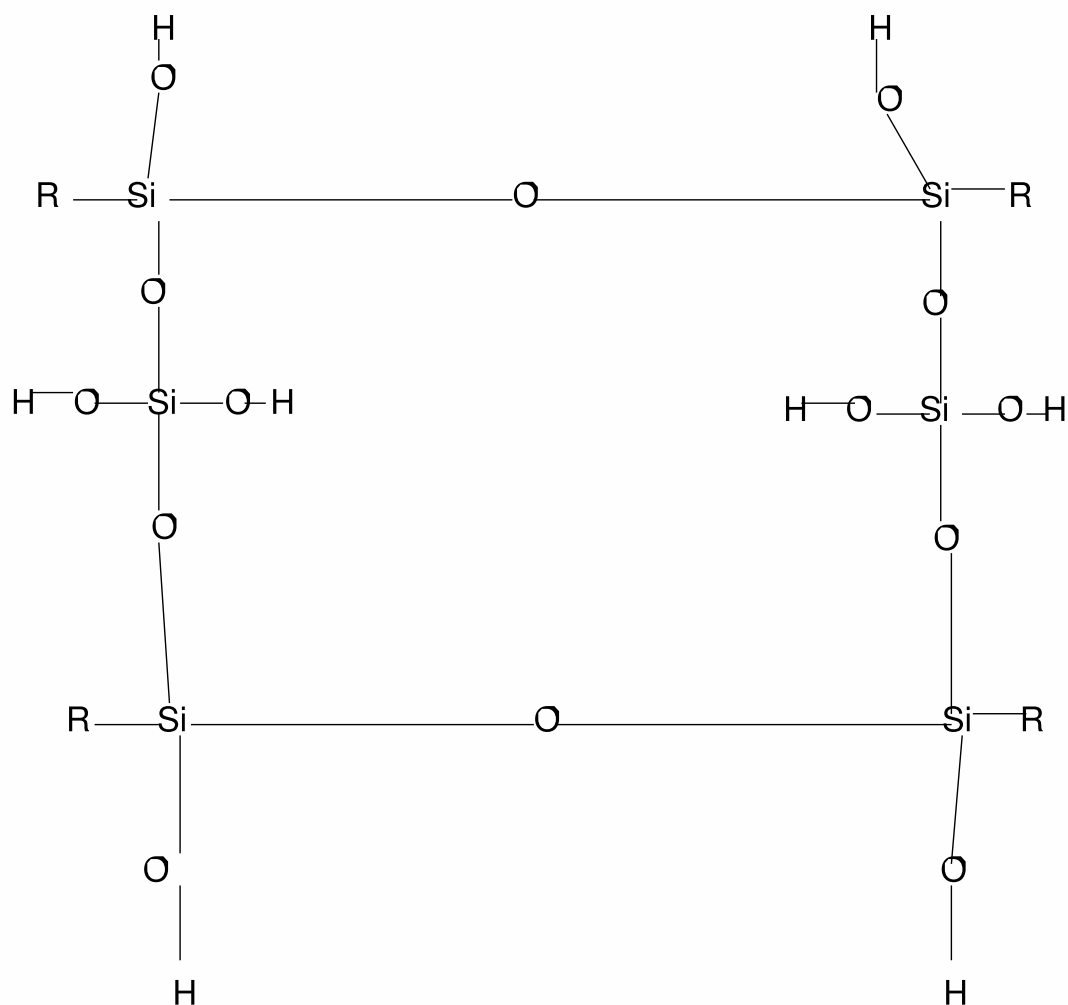


FIG. 1: Example of amorphous molecule with $R = H, CH_3, C_6H_5$

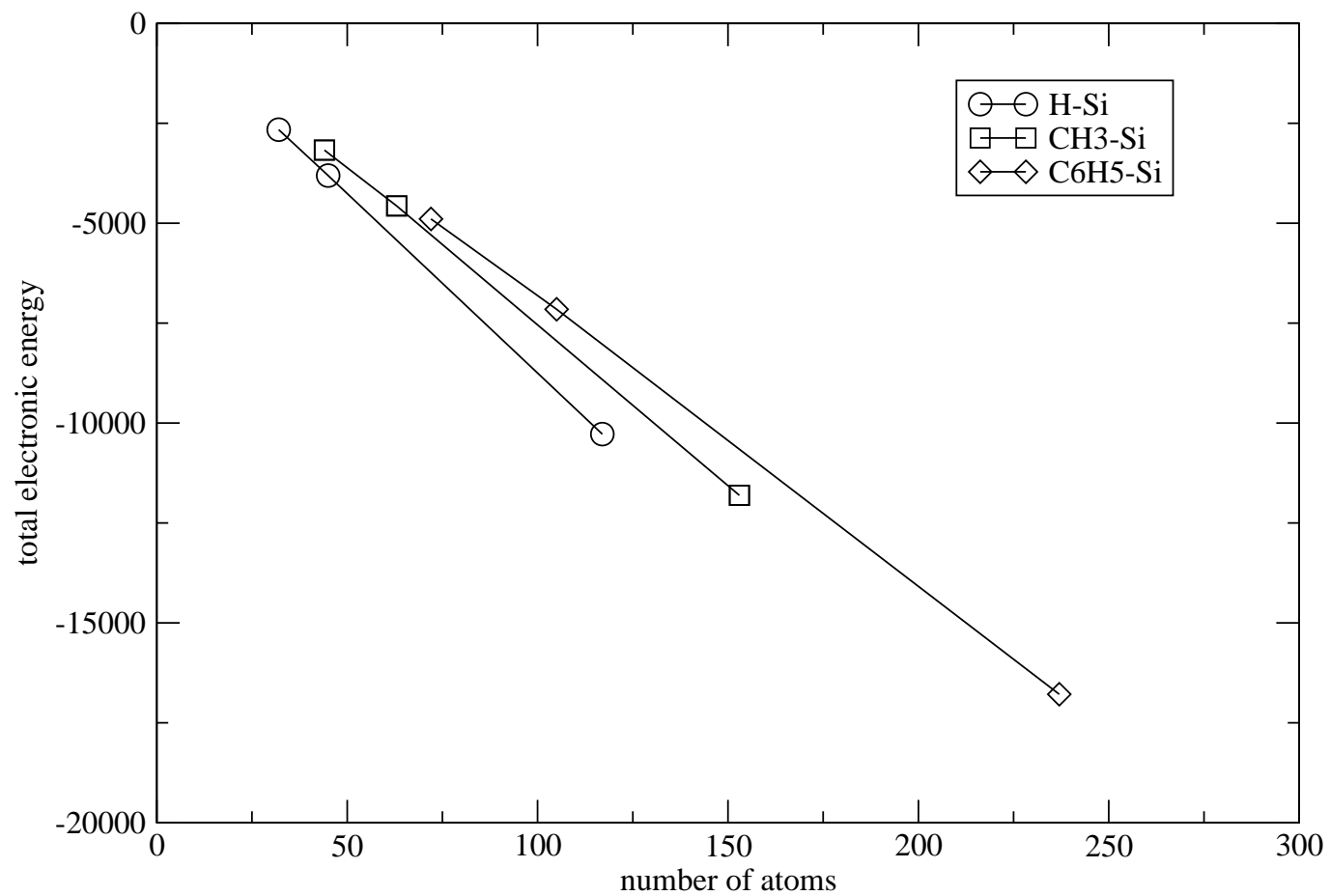


FIG. 2: Total electronic energy as a function of the number of atoms

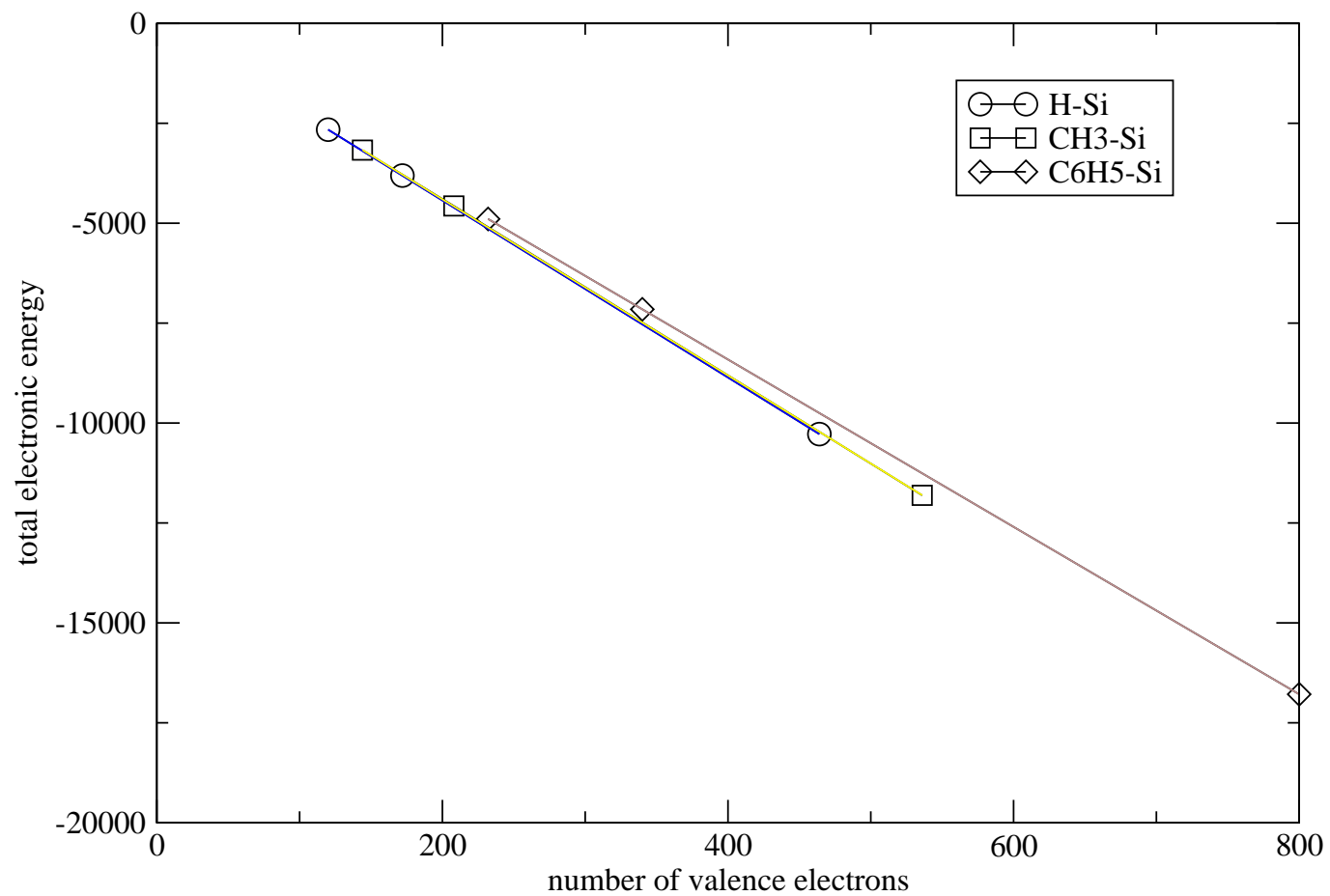


FIG. 3: Total electronic energy as a function of the number of bonds (π or σ)